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Coffee extract residue for production of ethanol and activated carbons

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ABSTRACT

Biomass as a waste product in the form coffee extract residue (CER) has been shown to have potential for the dual purpose of ethanol production and preparation of activated carbons. A straightforward method of direct hydrolysis and fermentation (DHF) is considered as the main option utilized in this study for the generation of fuel ethanol from the biomass waste. Factors such as loadings of *saccharomyces cerevisiae*, temperatures (21 and 30 °C) and substrate content were investigated to maximize the yield of ethanol. Ethanol production rates between 1.1 g and 0.70 g h^{-1} kg^{-1} without pretreatment and 2.7 and 2.3 g h^{-1} kg^{-1} dry substance with mild treatment were obtained, respectively. The CER was also used to prepare activated carbons using both chemical and physical activation methods. The effects of process parameters such as temperatures and concentrations of acid were varied and determined as to the yield, BET-surface areas and porosities of the final product. H_3PO_4 treatment at 600 °C and steam treatment at 700 °C show maximum surface area of >640 m^2 g^{-1} with increased total pore and micropore volumes.

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1. Introduction

Lignocellulosic biomass has the potential to be one of the major feedstocks for the production of bioethanol, recognized as the main replacement for the fossil fuel-based energy consumption in most IC engines. Ethanol as oxygenated fuel with almost 35% oxygen is an octane booster, which either in blended or pure form is believed to cut hydrocarbon and NOx emissions by 20% and CO_2 by 90% (Sheehan and Himmel, 1999). The global ethanol production volume stood at 85 GL in 2012, more than double the year 2006 and where the lions share was produced in the Americas (Renewable energy magazine, 2013). The main feedstocks for ethanol production are mostly derived from sugarcane and corn, although immense ethanol is anticipated to be produced using other biomass resources, such as agricultural waste and forest residues. Kim and Dale, 2004 showed that the global potential source of fuel ethanol from wasted crops and crop residues can culminate up to 491 GL y^{-1} and where the lignin-rich residue after fermentation might be used for generation of both 458 TWh of electricity and 2.6 EJ of steam. The same authors do also report that for a successful utilization of lignocellulosic materials, requirements such as high ethanol conversion, logistics and infrastructure for collection of the biomass, increase of thermal efficiency of electrical generation and steam are needed. By the same token lignocellulosic biomass can also be converted into activated carbons and thus another value-added product can be obtained from the same source. Pyrolysis of biomass by heat-treatment at higher temperatures generates char, oil and various gases to be used for sustainable and potential end products (Mythili et al., 2013). Thus, agricultural residues with virtually high carbon content can be readily processed to high surface area carbons with micro and mesoporous structures either by a physical or chemical activation as well as bioethanol (Jain et al., 2010; Neupane et al., 2011; Zahari et al., 2014; Chiu and Ng, 2012; Delivand et al., 2012). Activated carbons from waste tea, olive-seed, barley husks, cotton stalks and coffee residues were prepared with varying degrees of porosities and surface areas, depending on the type of chemicals, concentrations and temperatures used in the preparation steps (Gurten et al., 2012; Stavropoulos and Zabaniotou, 2005; Loredo-Cancino et al., 2013; Khenniche and Aissani, 2009; Reffas et al., 2010). Activated carbon (AC) is a versatile product and is widely used in different applications, such as adsorbents for waste removal and pollution control, water purification, dispersion of catalyst and catalyst support, electrochemical systems in batteries and supercapacitors, catalyst for oxygen reduction reaction in alkaline electrolyte, hydrogen storage, in food and beverage as well as steel industries, etc. (Kaouah et al., 2013; Liu et al., 2012; Ioannidou and Zabaniotou, 2007; Jordá-Beneyto et al., 2007; Sathiskumar et al., 2012; Spahis et al., 2008; Hung et al., 2009; Pirjamali and Kiros, 2002).

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Coffee usually packed in 60 kg bags is one of the second traded commodities after petroleum and is one of the most consumed beverages totaling about eight million metric tons in 2009/10 (ICO, 2013). According to the International Coffee Organization (ICO) the coffee per capita consumption in kg significantly varies from country to country, where Nordic countries are distinguished among the highest in the world and thus dispatching high volumes of coffee waste. Although there are different byproducts generated during the coffee processing steps from the green cherries to the brown beans after roasting, the largest residue is obtained after extraction of the soluble compounds. The coffee extract residue (CER) resulting in a ratio of between 2 and 4:1 to ground coffee obtained by filtration on a filter paper and through percolation by hot dripping water in a coffee machine is a substantial source of agricultural waste, which can be used in a number of application areas, such as substrate for mushroom cultivation, compost, direct removal of dyes, activated carbon and biosorbents, ethanol, as a fuel in industrial boilers for cogeneration of heat and/or electricity, biodiesel, briquettes and for a range of other chemical compounds (Mussatto et al., 2011a; Murthy and Naidu, 2012). Although the heating value of CER on dry basis 21.5 MJ/kg (Tsai et al., 2012) is comparable to fossil coal and other agricultural wastes and residues, the high humidity of the CER significantly decreases its overall heat content with eventual release of particulate matter and other gaseous byproducts if fired or co-fired with other precursors for district heating or electricity. Thus, search for other approaches to harness value-added chain of products from the disposal of thousands of tons of CER are essential for a sustainable environmental, cleaner and process technology solutions. Utilization of a product in its subsequent cycle of cradle-product-waste-product has a far reaching strategy in our holistic appraisal and solution of environmental significance. Ethanol and activated carbon are not only obtained from CER, but also other possible products can be extracted.

As the cellulose and hemicellulose content of CER is high (Mussatto et al., 2011b; Franca et al., 2005; Delgado et al., 2008) with relatively low ash content compared to other lignocellulosic biomass and due to the very small coffee particles (<1 mm original size) opening up for exposure to hydrolysis, direct hydrolysis and fermentation (DHF) has been applied for the first time in this study to produce ethanol. Pretreatment steps, which actually represent 20% of the total production cost (Chiaramonti et al., 2012) and seed culture of the microorganisms, are considered to increase the overall energy input and cost of ethanol production. Unless otherwise stated no physical or physicochemical and/or chemical pretreatment was used to separate the biomass components and eventually remove the lignin so that the extractable parts of the CER is accessible for the fermentation step. Factors such as substrate loading, amount of *saccharomyces cerevisiae* (baker's yeast), temperature and fermentation time that can affect the yield of ethanol have also been investigated. Furthermore, procedures using both chemical by impregnation with different concentrations of H_3PO_4 as well as physical by steam at high and different temperatures were employed to produce activated carbon from the CER. Various characterizations of the products were also conducted to substantiate the viability and validity in this two pronged approach and recovery of the lignocellulosic waste and byproducts.

2. Materials and methods

The coffee extract residue (CER) was obtained from the Division of Chemical Technology's coffee machines by discharging the filter paper into a flat tray of glass and was dried in an oven at 120 °C for 24 h as the water content of the residue exceeds more than 150%. This precursor is then used for further processing in the steps to follow for the generation of either ethanol or activated carbon. Bakers' yeast (Jästbolaget AB) from a local store, analytical grade 99.5% ethanol (Solveco AB), 85% H_3PO_4 (Merck), 1 M HCl (Merck) and N_2 (Aga Gas AB) were purchased for use in the respective products.

2.1. Batch fermentation

No special strain, seed culture, inoculation or immobilization of the *saccharomyces cerevisiae* was used in this study. A dry baker's yeast packed in 100 g portion having long durability was immersed in different amounts into 250 ml Erlenmeyer flasks used a batch reactor with 100 ml deionized water (DIW). The substrate loading (CER) was also varied to find optimum yield of ethanol under different reaction conditions (temperature, fermentation time and boiling of water with the substrate). Prior to the start of each experiment, the reactor was purged and blanketed for 2 min by nitrogen gas for removing air so that the reaction takes place under anaerobic conditions. A loop trap for venting liberated CO_2 during the reaction was also connected to the reactor. In order to increase the nutrient transfer between the substrate and yeast cells, a Teflon magnetic stirrer at 30 rpm throughout the DHF was used and the temperature was adjusted by a water bath. The liquid phase of the fermented broth was filtered and placed in vials for analysis of ethanol concentration. A GC (Agilent 6890) fitted with split inlet and flame ionization detector (FID) and an HP-FAAP polyethylene glycol TPA column was used for quantitative analysis of the products. The oven temperature varied from 70 to 200 °C at different ramps and hold-up times and the carrier gas was helium. Calibration of the GC was done by pure (99.5%) ethanol with dilute and different concentrations to be fitted to the different peak areas obtained for the samples.

2.2. Preparation of activated carbons

The experimental procedures consist of evaluating and comparing the surface properties of the activated carbons prepared by the chemical activation using phosphoric acid and physical activation using steam. During the chemical activation process 50 g of the dry CER samples were placed in a beaker and impregnated by adding adequate volumes of H_3PO_4 at different concentrations: 30, 40 and 50% so that the samples are entirely soaked. After this step, the samples were sonicated for two hours in an ultrasound bath (40 kHz) in order to allow the dehydrating agent to diffuse into and within the fine particles of the biomass. The samples used for preparation of activated carbons are denoted by CA or TA for chemical or thermal activation followed by 3 (30%), 4 (40%) or 5 (50%) for the concentrations of H_3PO_4 and ultimately by the heat-treatment temperatures of 500, 600, 700 and 800 °C. The impregnated samples were then dried at 120 °C for 24 h to be pyrolyzed in a horizontal tube furnace. Once the furnace achieved the set temperature, the sample contained in an inconel boat was introduced in the heating zone for the activation to take place for one hour. 500 °C, 600 °C and 700 °C were studied as the carbonization temperatures under continuous N_2 gas flow for removing the volatile components from the charred residue and preventing any further reaction with oxygen. The aqueous reaction product moving along the cooling zone (0.5 m in length) of the furnace was trapped in a gas washing bottle. At the end of the activation period, the sample was cooled down by a flow of water in a cooling zone and in the presence of nitrogen. The sample was then pulverized in a coffee mixer, washed several times by deionized water followed by soaking in 1 M HCl, blended by a magnetic stirrer for half an hour in order to remove any soluble components of inorganic and other ash components. In the final step the activated carbon was rinsed in deionized water, filtered and dried at 110 °C for 24 h.

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The physical activation was conducted at three different temperatures (600, 700 and 800 °C). Prior to the introduction of 50 g sample of the CER in the hot zone of the furnace, the furnace was purged by a flow of nitrogen to remove oxygen. The flow rate of deionized water was 20 ml/h, where it was injected in the cooling zone, moved through the tubing and vaporized at the rear side of the furnace. The steam to nitrogen volume ratio was held constant at 1:2 during the two hours of carbonization. All the other procedures for the after treatment of the final activated carbons were similar to the procedures of those described above.

The activated carbon yield was calculated by the following equation:

$$X(\%) = \frac{AC \times 100}{CER} \tag{1}$$

where AC is the weight of the activated carbon after washing and drying and CER is the coffee extract residue.

The degree of burn-off is similarly given by the percentage of mass loss after the whole activation step, while the ash content is the difference between the weight after carbonization and the remaining mass after washing with HCl and drying.

2.2.1. Materials characterization

The total surface area (BET-area), pore size distribution and pore volume are important properties for the assessment of the surface characteristics of activated carbon and similar materials. These properties were determined for the different activated carbons obtained by both the chemical and physical activations by adsorption isotherm of nitrogen at liquid nitrogen temperature (−196 °C) at different partial pressures (ASAP-2000 Micromeritics) according to the Brunauer Emmett and Teller (BET) equation. Small samples of the activated carbons (0.3–0.6 g) were loaded into a glass holder, degassed at 250 °C under vacuum until equilibrium was achieved and were then analyzed. The t-plot as a function of the thickness of the adsorbed layers to the relative volume (V/Vm) and relative pressure (P/Po) defines the micropore volume and microporous surface area, while pore size distributions were obtained from the adsorption branch of the isotherms by Barrett–Joyner–Halenda (BJH) method. Scanning electron microscopy (SEM) on the chemically activated samples was carried out for characterization of the microstructure and particle morphology by a high resolution Gemini, Zeiss-Ultra 55.

3. Results and discussions

3.1. Ethanol production

Saccharomyces cerevisiae (baker's yeast) due to its successful use in different biotechnological processes and industries such as in bakery and brewery is an efficient microorganism. However, limitations for the fermentation of lignocellulosic hydrolysate products, mainly pentose and other components have been found to be the main hurdles in maintaining higher yields of ethanol. Possible genetic modification by recombinant DNA technology and comprehensive genome information has currently made this microorganism more attractive to increase ethanol production (Ostergaard et al., 2006). In this study, microorganisms without any prior modification were used in DHF for the conversion of the soluble products of cellulose and sugars of CER to ethanol. Although in most ethanol production processes different treatments and temperatures are needed for separate hydrolysis and fermentation, operation under distinct and lower temperatures of the CER in the presence of the free *saccharomyces cerevisiae* is desirable from process point of view and cost effectiveness.

Fig. 1 shows ethanol production at both 21 and 30 °C with varying CER loading. In both temperatures, the ethanol produced increased and reached a maximum at a CER loading of 16 g, where the amount of water (100 ml), yeast (1 g) and the DHF time (48 h) were kept constant. The increase of temperature affects the ethanol production slightly at both low and high CER loading, as the fermentation and growth rate of the cells seem to be favorable at 30 °C showing more than 9% in yield compared to the lower and intermittent amount of the substrates. Temperature of free *s. cerevisiae* for fermentation at 30 °C has also been given as the optimum by the supplier's product description. The ethanol production seems to subside either at lower or higher CER loading, which might be ascribed to lower activities of the yeast to maintain the metabolism and/or underutilization of the nutrients exceeding the concentration or population level of the cells. Higher substrate amount may also impede the fermentation process due to formation of higher concentration of ethanol and byproducts that are unfavorable to the cells. Thus, a balance between suitable substrate and yeast loading under constant stirring fulfills the extent of ethanol production, where the carbon dioxide formed during the reaction is continuously vented. The ethanol production rate, therefore varies between 1.1 g and 0.70 g h^{-1} kg^{-1} dry substance, showing relevance for a lignocellulosic material, where no pretreatment steps were conducted. Fermentation of the lignocellulosic hydrolysates by microorganisms would mean conversion of both hexose sugars of glucose, mannose and galactose as well as the pentose sugars of xylose and arabinose. However, yeast cells are not capable to make use of the pentose sugars and thus a significant amount of sugars remains unutilized (Margeot et al., 2009).

Fig. 2 shows the production of ethanol using different amounts of *s. cerevisiae* (1, 2 and 3 g) as function of fermentation time, at both 48 h and 72 h as well as one at 140 h under a constant CER loading of 16 g, 100 ml water and at 30 °C. From the results, it is evident that the more the amount of yeast, the higher is the ethanol produced, showing higher metabolism and utilization of the CER in the presence of higher concentration of the cells. Thus, there is a positive correlation between the amount of yeast and ethanol production. Likewise, lower fermentation time at 48 h compared to 72 h shows higher ethanol content. Increasing the fermentation time might lead to a slow down of cell growth and cell density as per the substrate loading in the batch reactor, where dissociation and formation of other byproducts might take place. However, the trend of ethanol production at 72 h is similar to the fermentation time at 48 h as increasing the amount of yeast depicts increased ethanol production, albeit with the production rate declining by an average of 13% compared to 48 h. No ethanol is produced upon extending the fermentation time to 140 h, which might be explained by the release of inhibitors caused either by the disruption of yeast cells by ethanol and/or formation of other chemical compounds. The performance of *s. cerevisiae* and its specific growth

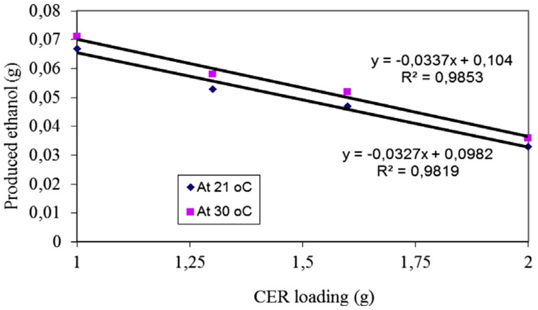

Fig. 1. Ethanol production at different substrate loading and temperatures.

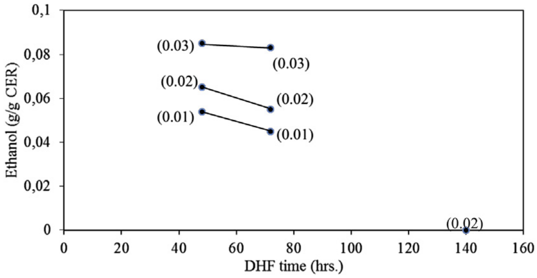

Fig. 2. Production of ethanol with different amounts of yeast cells in ( ) and fermentation time.

in lignocellulosic substrates depends on the concentrations of various weak acids, furan derivatives and phenolic compounds, which originate from the biomass components (cellulose, hemicellulose and lignin). High concentrations of these species limit the performance and efficient use of the hydrolysates for ethanol production from lignocellulosic materials (Palmqvist and Hahn-Hagerdal, 2000; Klinke et al., 2004).

Fig. 3 shows the ethanol produced after cooking pretreatment of the CER in 100 ml of deionized water of a dry weight of 16 g at 95 °C for 30 min, where the hydrolysate was extracted and underwent fermentation. The aqueous phase and the solid CER were fermented separately for 48 h with different loadings of yeast and at a constant temperature of 30 °C. Interestingly, the ethanol produced under such conditions and the combinations thereof far exceeded the untreated samples shown in the previous results. A combined ethanol production rate of 2.3 and 2.7 g h^{-1} kg^{-1} dry substance, respectively, showed a linear increase in relation to the weight of yeast and the aqueous and solid fractions.

Though pretreatment steps such as physical, physicochemical, chemical and biological processes for modification of the surface properties of lignocellulosic materials are used (Chiaramonti et al., 2012; Sun and Cheng, 2002), cost-effective and straightforward methods are preferable to cut the energy requirements due to down stream and overall plant operation process. Hamelinck et al., 2005 analyzed the technical performance as related to current available technology based on the dilute acid hydrolysis and found that the efficiency is about 35% (HHV) for conversion of biomass to ethanol, while improvements in pretreatments and biotechnology with process combinations may bring the ethanol efficiency to 48%. In order to utilize lignocellulosic biomass and its fermentability, pretreatments or detoxification (physical, chemical or biological) methods are used to increase the surface area, bulk density and reduce the crystallinity of the cellulose (Prasad et al., 2007). Inevitably, mild pretreatments or direct hydrolysis are preferred for the first saccharification step so that formation of other compounds that may inhibit the microorganisms as well as the number of reactors are limited as these factors are related to the overall investment costs. The combined cooking with subsequent fermentation of both the aqueous and solid phases showed in Fig. 3 resulted in an overall ethanol yield of 0.22 L kg^{-1} and 0.18 L kg^{-1} dry CER for the higher and lower yeast loading, respectively. These values are in close proximity to the yields of ethanol produced from lignocellulosic waste crops as reported by Kim and Dale (2004).

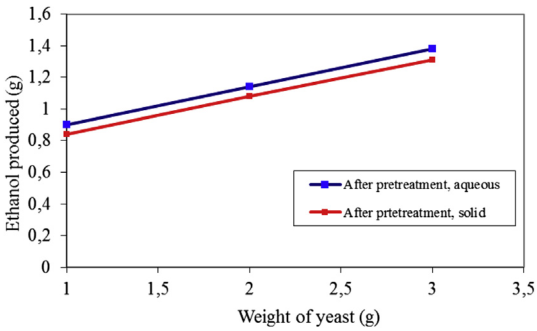

Fig. 3. Production of ethanol after cooking treatment of both the aqueous phase and solid residue.

Coffee beans are normally processed industrially by roasting or by mild torrefaction at temperatures between 180 and 240 °C, where substantial part of the moisture contained in the beans and volatile compounds are degassed and released along with the removal of the protective cover of the lignin and hemicellulose. This is followed by comminution with milling where fine powders are obtained for further brewing in most cases by filtration. After filtration the coffee extract residue (CER) does contain an ample amount of the lignocellulosic compounds, which still have readily accessible C6 sugars (hexoses) and other fermentable components. Thus, CER disposed as a waste might accrue the positive outcome in a product's lifecycle and become a potential source for the production of ethanol. Its thermal treatment in the form of roasting and with surface properties due to destruction of the cell wall structure makes it highly exposed to the ease of fermentation with higher yields of ethanol.

Down stream processes for utilization of the byproducts is important, especially in the ethanol fermentation industry using appropriate technologies for cleaner production. The concurrent production of stillage should be addressed where big volumes are dispatched, impacting pollution problems. Various separation technologies after distillation and making use of the stillage by recycling the water by ultrafiltration with ceramic membranes, generation of biogas by anaerobic digestion, extraction of organic acids and sugar alcohols were reported by Kim et al. (1997), Wilkie et al. (2000), Kaparaju et al. (2009), Mussatto et al. (2011b). Similarly, the biooil co-produced during pyrolysis of CER for the production of activated carbons as described in the following subsection may be used as a replacement for fossil fuels and other usable and valuable bulk products (Mythili et al., 2013; Kajaste, 2014).

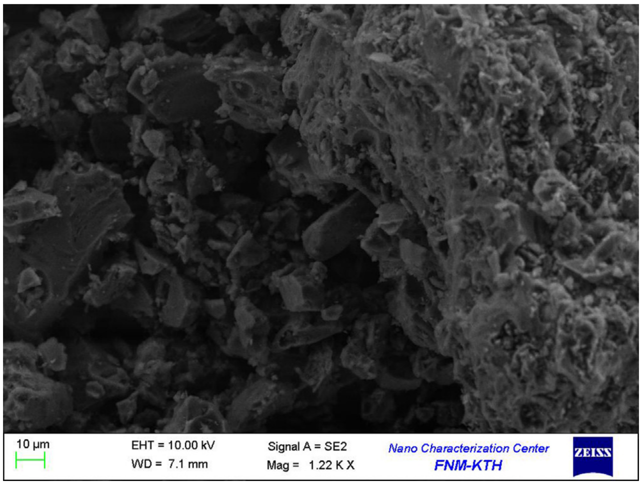

Fig. 4. Scanning electron microscopy of the chemically activated carbon (40% H_3PO_4 at 600 °C).

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3.2. Activated carbon

Fig. 4 shows a SEM image of a sample of highly aggregated carbon powder containing both rough and smooth surfaces, representative for most of the activated carbons from CER. The particles are not of uniform size, though milling or grinding after the activation steps were conducted with all the samples.

Table 1 shows the effect of the chemical and physical activations carried out at different temperatures and concentrations of phosphoric acid and steam on the yields of activated carbon, burn-offs and ash contents. The carbon yield (%) obtained by the chemical activation are around 32–50% with corresponding burn-offs. However, the yields achieved by the physical activation (12–18%) are much lower than those obtained by the chemical activation.

The general trend of the CER samples impregnated with the different concentrations of the dehydrating agent is that the yield at similar temperatures is high for the lower concentrations, decreases to some level at the intermediate temperature and then increases at higher temperatures. The insertion of phosphoric acid in the lignocellulosic (cellulose, hemicellulose and lignin) layers leads to the attack of the structure by dehydration reactions during the heat-treatment, release of water vapour and other volatile compounds form the surface and modification of the structure by the insertion of functionalized surface groups. The cross-linking reactions of the carbonaceous material, oxygen, hydrogen and nitrogen-containing compounds during pyrolysis result in a charred residue with high porosities and surface areas. The liberation of volatiles and tar components as well as oxidation products of carbon from the mixtures are dependent on the concentration of the activating reagent, residence time, temperature, which are considered to be important parameters for the creation of activated carbon in the process (Williams and Reed, 2006).

The reaction of biomass with H_3PO_4, having different conjugate bases can promote bond cleavage reactions and formation of crosslink by combining with the lignocellulosic polymers. Phosphate linkages, such as phosphate and polyphosphate esters (Kalderis et al., 2008) can serve to connect and bind strongly to the biopolymer matrix and thereby increase the retention of these compounds within the structure. Thus, the yields of the activated carbons by chemical activation are significantly higher than by physical activation. Higher burn-offs (<80%) and thus fewer yields were achieved (ca 20%) by the physical activation due to high exposure and reaction of the polymeric biomass with steam. Likewise, the ash content by chemical activation shows almost similar characteristics with less variation between 9 and 11%, regardless of the temperatures and/or concentrations of phosphoric acid, as the components to be washed out after the treatment do not vary significantly. However, the conditions for the reaction with steam are different showing an increase of the loss of the volatile materials and much more oxidation of the carbonaceous components of the CER with an increase of the ash content with temperature.

Total surface areas, pore diameters, total pore volumes and micropore volumes together with the type of the treatment methods, phosphoric acid concentrations and temperatures are shown in Table 2. The specific surface areas were found to increase initially from the lower concentrations of H_3PO_4 to the intermediate concentration and temperature at 600 °C reaching a maximum of 696 $m^2\ g^{-1}$, whereas steam activation showed 641 $m^2\ g^{-1}$at 700 °C. The surface areas are much higher than those activated carbons from coffee residues treated by $ZnCl_2$ as reported by Boonamnuayvitaya et al. (2005) but less than those obtained by the combination of $ZnCl_2$–N_2–CO_2. In a similar work but with impregnation ratios of H_3PO_4 between 30 and 180 wt.% to the weight of coffee grounds and at 450 °C, Reffas et al. (2010) showed surface areas as high as 925 $m^2\ g^{-1}$ and with almost complete mesoporous volume for the higher concentration. The decrease in surface area at high temperatures for the steam treatment and higher concentrations of H_3PO_4 might be due to the breakdown, restructuring and constriction of the pore walls and pore apertures of the activated carbons. The total pore volume and the micropore volume increased following the same relationships as the surface areas, leading to 0.59 and 0.101 $cm^3\ g^{-1}$ for the chemically activated samples whereas physical activation of the samples at 700 °C resulted in the generation of highly micropore volume of 0.232 and total pore volume of 0.33 $cm^3\ g^{-1}$, respectively. Comparison among both activation methods have also shown that the more the burn-off (Table 1), the higher is the micropore volumes produced, which is in line with the report by Williams and Reed (2006). Phosphoric acid might be incorporated as a melt in the form of phosphorous pentoxide in the carbon structure undergoing phase changes from solid to vapour at the high temperatures and thereby blocking the creation of higher volumes of mesopores and micropores.

Activated carbons have characteristic porosities, which depend on the size (micropore < 2 nm, mesopore 2–50 nm and macropore > 50 nm) and pore size distributions and as such are distinctive for application in adsorption processes for gases, liquids and solids. Fig. 5 shows the nitrogen adsorption–desorption isotherms in terms of adsorbed volume ($cm^3\ g^{-1}$) and relative pressures (P/Po), having Type IV isotherms for the chemically activated carbons (Fig. 5a) and Type I for the physically activated carbons (Fig. 5b). Impregnation of the biomass with phosphoric acid and pyrolysis result in eventual ejection of the volatile components resulting in opening up and widening of the pore structures as also

Table 1
Effect of chemical and physical treatments of CER on the activated carbon.

Type of treatment	Yield (%)	Burn-off (%)	Ash content (%)
CA-3-500	39.0	61.0	10.3
CA-4-500	32.3	67.7	10.5
CA-5-500	36.6	63.4	10.4
CA-3-600	49.6	50.4	9.7
CA-4-600	34.9	65.1	10.4
CA-5-600	41.0	59.0	10.3
CA-3-700	48.1	51.9	9.9
CA-4-700	36.8	63.2	10.7
CA-5-700	46.6	53.4	9.8
TA-600	18.4	81.6	19.5
TA-700	13.4	86.6	21.1
TA-800	12.7	87.3	23.4

CA-chemical activation, TA-thermal activation.

Table 2
Specific surface area, pore diameter, pore volume and micropore volume of the activated carbons.

Sample	*St*	*D*	*Vt*	*Vmic*
	($m^2\ g^{-1}$)	(Å)	($cm^3\ g^{-1}$)	($cm^3\ g^{-1}$)
CA-3-500	523	27.5	0.36	0.067
CA-3-600	531	26.8	0.42	0.070
CA-3-700	584	28.8	0.47	0.080
CA-4-500	605	33.5	0.51	0.091
CA-4-600	696	33.7	0.59	0.101
CA-4-700	421	35.8	0.38	0.053
CA-5-500	233	38.1	0.22	0.015
CA-5-600	360	33.2	0.30	0.031
CA-5-700	352	27.1	0.24	0.046
TA-600	567	20.4	0.29	0.214
TA-700	641	20.6	0.33	0.232
TA-800	533	21.9	0.29	0.194

CA-chemical activation; TA-thermal activation; *St*-total specific surface area; *D*-pore diameter; *Vt*-total pore volume; *Vmic*-micropore volume.

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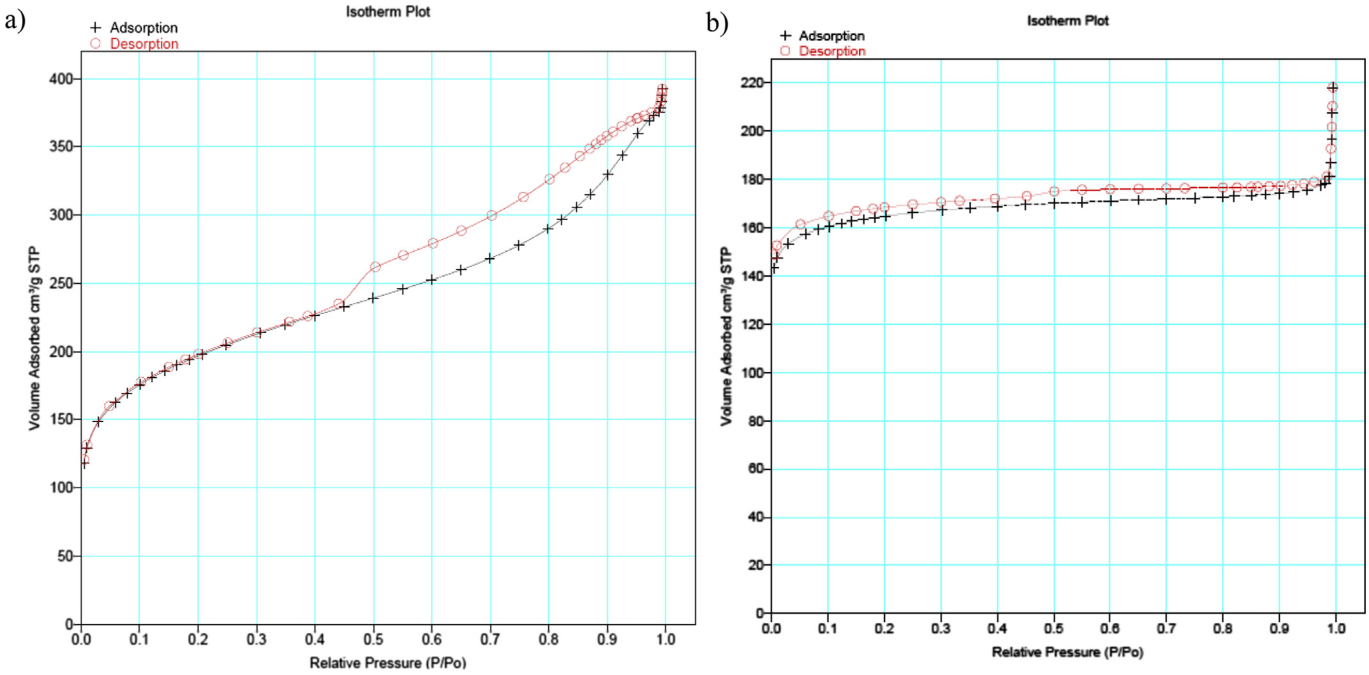

Fig. 5. Adsorption-desorption isotherms of nitrogen; a) chemical activation (40% H_3PO_4 at 600 °C) b) physical activation at 600 °C.

shown in the pore diameters enlisted in Table 2. Type IV in Fig. 5a with the typical adsorption–desorption isotherms shows a hysteresis loop for a surface composed of mesoporous structure, implying higher retention volumes for the adsorbate. The physically activated carbons have predominantly microporous structures with less or no hysteresis loop with curves that are prone to domination at the edges. Thus, the effect of impregnation of higher concentrations of phosphoric acid and lengthy pyrolysis time might induce increased removal of the surface and pore walls by creating wider pores with less pronounced surface areas. However, in the case of the physical activation surface and pore shrinkages gave rise to enhanced micropores with higher surface areas approaching maximum at the intermediate temperature of 700 °C.

4. Conclusion

This work demonstrates that coffee extract residue can be used for the generation of two distinct products, viz. ethanol and activated carbons. The prospective end-use of abundant waste and waste feedstocks of lignocellulosic biomass is attractive and promising for the production of both fuel and adsorbent.

A straightforward method for ethanol production by *saccharomyces cerevisiae* using different amounts, temperatures, substrate loading, fermentation time and with or without mild treatments was carried out. Higher yields of ethanol were obtained as the cell walls of the biomass with small particle sizes were exposed for the direct hydrolysis and fermentation. Based on the experiments, the optimal fermentation was determined as follows; temperature 30 °C, yeast 30 mg g^{-1}CER and a combined aqueous phase after cooking and solid residue fermentation after treatment. The result also conveys that there is a potential for ethanol production if conditions for further extraction of the hexose and pentose sugars are increased.

Highly developed mesoporous and microporous structures of activated carbons were prepared by both chemical and physical activation of the coffee extract residue. Depending on the activation method, concentration of acid and pyrolysis temperature, different surface areas and yields were obtained for specific use of the activated carbons as adsorbents. The waste CER is a potential source and can find applications as low cost alternative for the removal and adsorption of solid, liquid and gaseous contaminants.

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